On the Fluorescence of Æsculin.

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I. *Introduction.*

In a paper published in 1918, describing observations on thin films of fluorescent solutions, Perrin* presented an extremely interesting explanation of fluorescence. According to him, organic substances when fluorescing are in the process of being destroyed. This destruction he considers to be the cause of the fluorescence. The molecule of the fluorescent substance is supposed not to possess a permanent ability to emit light under stimulation, but to have the power to give out light at the moment of its transformation. On being transformed it is rendered incapable of further fluorescence. Since the molecules of all the fluorescent substances studied by him contained one or more benzene rings, he made the suggestion that fluorescence in the cases investigated was probably due to the rupture of these rings.

R. W. Wood† has also published recently an account of an investigation on the destruction of the fluorescent powers of certain solutions by exposure to sunlight. He found that the fluorescent solutions studied by him could be transformed into coloured non-fluorescent liquids that gave absorption spectra decidedly different from the original solutions. Prolonged exposure to sunlight, moreover, rendered his solutions colourless. In particular, he found that solutions of rhodamine could be bleached without the emission of fluorescent light by maintaining them at a temperature of 100° C., a result which would indicate that the transformation of the molecules of fluorescent solutions may not be as intimately connected with the phenomenon of fluorescence as Perrin has supposed.

In order to add, if possible, to our knowledge of the subject, some experiments were recently made by the writers on the fluorescence of æsculin, and in the course of these experiments it was found that solutions of æsculin could be rendered non-fluorescent not only by exposure to ultra-violet light but also by passing through them in darkness ozonised oxygen. The transformed solutions, too, were found to possess an absorption spectrum different from that of the original solutions.

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* Perrin, 'Ann. d. Physique,' (9), vol. 10, pp. 133–159, Sept.-Oct. (1918).

† R. W. Wood, 'Phil. Mag.,' vol. 43, pp. 757–765 (1922).

It is known that when the fluorescent power of æsculin is destroyed by the addition of a little acid the fluorescent power of such solutions can be restored by a few drops of an alkali, such as potassium hydroxide. In the case of the solutions of æsculin transformed in our experiments by ultra-violet light or by ozone, it was found that the fluorescent power could not be restored by the addition of the hydroxide. It was also found that solutions of æsculin freed from air and sealed up in evacuated glass tubes could be made to fluoresce for long periods by exposure to ultra-violet light without losing to any measurable extent their power to fluoresce.

When transforming solutions of æsculin, by passing through them in darkness ozonised oxygen, it was found that the transformation was accompanied by the emission of an extremely faint bluish white light.

II. *Apparatus and Method.*

In transforming aqueous solutions of æsculin ($C_{15}H_{16}O_9$) they were exposed in test-tubes of glass or quartz to the light from a powerful quartz mercury-arc lamp. At regular intervals during the exposure the solutions were removed and their fluorescent powers compared with that of the original unexposed stock solution. The quartz mercury-arc lamp used was 75 cm. in length and carried about 10 ampères. Although the light emitted by the lamp was very intense, the solution suffered only a slight rise of temperature during exposure, the distance between the lamp and the test-tube being generally about 15 cm. or 20 cm.

A Nutting spectrophotometer was used to measure the intensity of fluorescence, and the method of using it is shown in fig. 1. The light from a self-regulating carbon-arc lamp (A) was reflected downwards by a mirror (D) into two cells (H) containing the fluorescent solutions to be compared. The fluorescent light from those cells passed through stops (F) and entered the

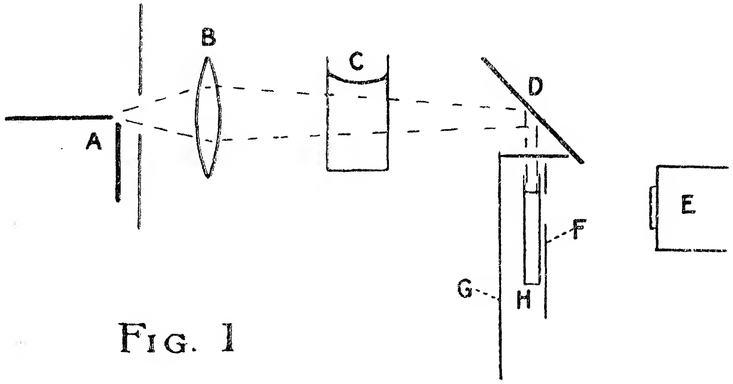

FIG. 1

openings of the photometer in a direction at right angles to the final direction of the exciting beam. By varying the height of the stops the fluorescence at any depth of the liquid could be measured. In our experiments the stops were 4 mm. in width, and the fluorescent powers of the first 4 mm. of the solutions were compared. Solutions sufficiently dilute to show no appreciable absorption over the area investigated were used, so that images uniformly luminous were seen in the photometer. A screen at G served as a dark background for the fluorescent light and kept any stray light emitted by the carbon-arc lamp from entering the photometer directly. The exciting light from the carbon arc was passed through a nickel oxide glass filter, and as a result was limited to the region $\lambda = 3342$ A to $\lambda = 4078$ A with a faint radiation in the extreme red.

In a test made with pure distilled water in the cells used for holding the fluorescent solutions, visible light could only just be detected in the photometer, and that only when the eye was rested in the dark before making the observations. Light of this character was therefore neglected in making comparisons of the intensities of the fluorescent light of the solutions. As the intensity* of the fluorescent light was found to vary directly with the intensity of the exciting light, any slight variation in the intensity of the light from the arc was assumed to affect both the standard æsculin solution and the one under test in the same way.

III. *Sensitivity of Photometer.*

In some preliminary experiments made to test the sensitivity of the photometer, the standard solution was taken as 4/100,000, and it was found that the intensity of fluorescence of solutions as dilute as 1/10,000,000 could be detected and measured.

IV. *Fluorescence and Absorption Spectra of Solutions.*

In an experiment to photograph the fluorescence spectrum of æsculin dissolved in water, the light from a quartz mercury-arc lamp was projected into the solution contained in a fused quartz tube, and the fluorescent light emitted from the tube at right angles to the direction of the exciting light was passed through a quartz spectrograph. The fluorescent spectrum consisted of a broad continuous band, extending from about $\lambda = 5461$ A to $\lambda = 4078$ A.

With long exposures to ultra-violet light the æsculin solutions were transformed from a colourless liquid that exhibited fluorescence into one of a pale amber tint that was non-fluorescent. The absorption spectrum of the fluorescing æsculin solutions was characterised by one broad absorption band in the extreme ultra-violet and a second broad one with maximum absorption close to λ = 3400 A. In the absorption spectrum of the transformed æsculin solutions the broad band with maximum absorption at λ = 3400 A was absent. This result indicates that the light responsible for the excitation of the fluorescence of æsculin was practically confined within the limits fixed by the transparency of the nickel-oxide glass filter. The result also shows that in the fluorescence of æsculin solutions we have a definite illustration of the applicability of Stokes's law.

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* R. W. Wood, *loc. cit.*

By testing solutions that were exposed for different periods attempts were made to see if spectra could be obtained with absorption bands differing slightly from those of the spectrum of the stock solution, but no such spectra were obtained. In this regard æsculin seems to differ from some of the substances studied by R. W. Wood, for, in his experiment on absorption spectra, he appears to have found that, in the transformations which he brought about, an intermediary product was obtained, for which the absorption spectrum was slightly different from that of his stock solution, as well as from that of the completely transformed one.

V. *Experiments on Fluorescence excited by Ultra-Violet Light.*

In the first set of experiments observations were made on the fluorescent powers of solutions of æsculin in water of different concentrations, the strongest solution used being that of four parts by weight of æsculin to 10^5 parts of water. The results of these observations are shown graphically in fig. 2. From the curve it will be seen that for very dilute solutions the

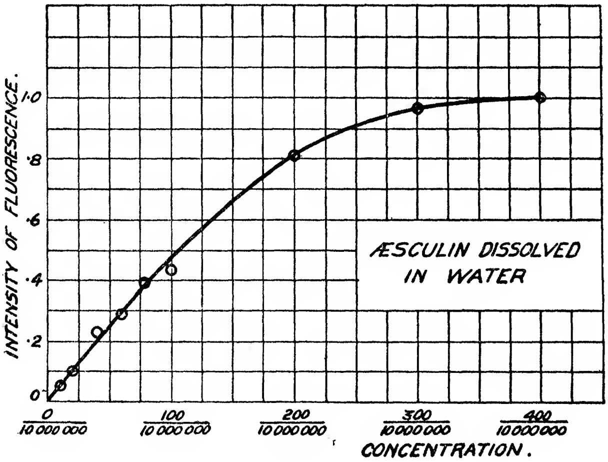

Fig. 2.

fluorescent power was directly proportional to the concentration. For solutions stronger than one part in 10^5 of water this law no longer applied. With solutions having four parts of æsculin to 10^5 parts of water the intensity of the fluorescence reached approximately its maximum value, a result that was in accordance with the observations cited by Perrin.

In a second set of experiments solutions of æsculin in water having the same initial concentrations were placed in tubes of quartz and of glass, having approximately the same thickness of wall, and these were exposed at the same distance from the lighted mercury-arc lamp. The intensity curves for the fluorescence of the solutions in the glass tubes were found to have the same form as those of the solutions in the quartz tubes, but the rate of decay of the fluorescent power of the former was only about one-half of that of the latter. As the glass did not transmit any radiation of wave-length shorter than $\lambda = 3342$ A, it would appear that radiations from the quartz mercury-arc lamp, of wave-lengths shorter than $\lambda = 3342$ A, were at least as effective in transforming the æsculin as the radiations from the lamp having wave-lengths longer than $\lambda = 3342$ A. Illustrations of the curves of decay for the two cases are shown in fig. 3.

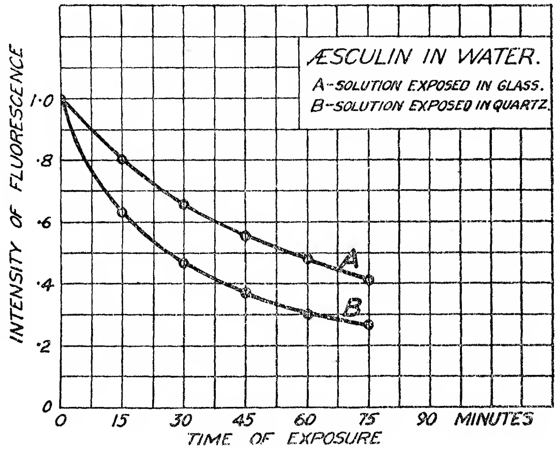

Fig. 3.

In a third set of experiments samples of the stock solution were diluted to the same amount; one by the addition of distilled water, and others by the addition, in varying strengths, of solutions that had completely lost their power of fluorescence through exposure to ultra-violet light. On testing these diluted solutions it was found that they all exhibited the same fluorescent power. From this result the conclusion was drawn that the fluorescent power of untransformed molecules of æsculin in solution in water was not affected by the presence in the solution of molecules of the æsculin that had undergone transformation.

In a fourth set of experiments a solution contained in a glass tube, and having an initial strength of four parts of æsculin in 10^5 parts of water, was exposed for 90 minutes to the ultra-violet light from the powerful quartz mercury lamp referred to above. At intervals during this period the fluorescent power of the solution was measured. At the end of the 90 minutes of exposure the solution was placed in a cabinet in a darkened room for a period of 20 hours, after which the exposure was continued for 45 minutes more, making 135 minutes in all. The solution was then placed once more in the cabinet in the darkened room for 170 hours, and at the end of this time its fluorescent power was again measured. The results of these measurements are shown graphically in fig. 4.

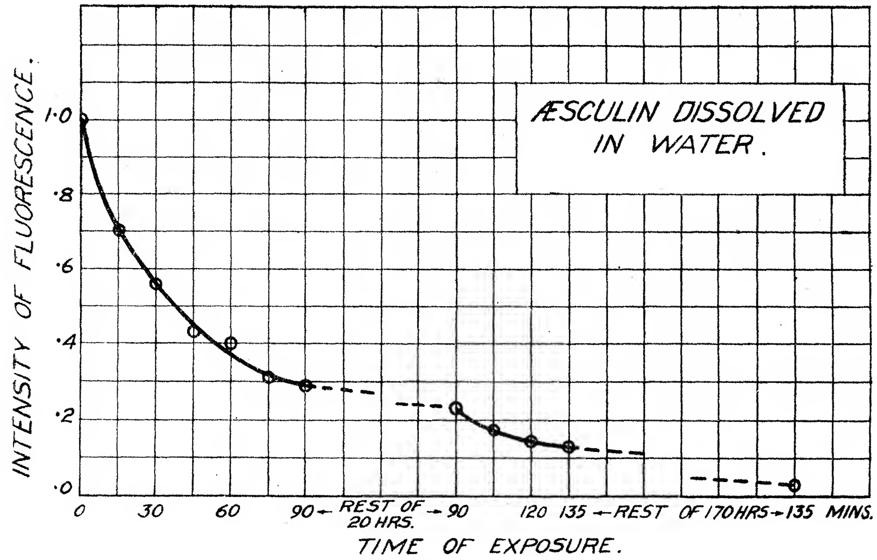

Fig. 4.

By assuming, as a result of the third set of experiments, that the fluorescent power of a solution was not affected by the presence in it of transformed molecules of æsculin, it was possible from the results, to calculate the concentration of untransformed æsculin in the solution at various times during its exposure. The values of these concentrations are shown in fig. 5. From these values the changes in concentration per second were calculated and the percentage changes of the untransformed æsculin in solution were deduced. Curves representing them are given in fig. 6. From these latter curves it will be seen that the percentage rate of transformation decreased rapidly in

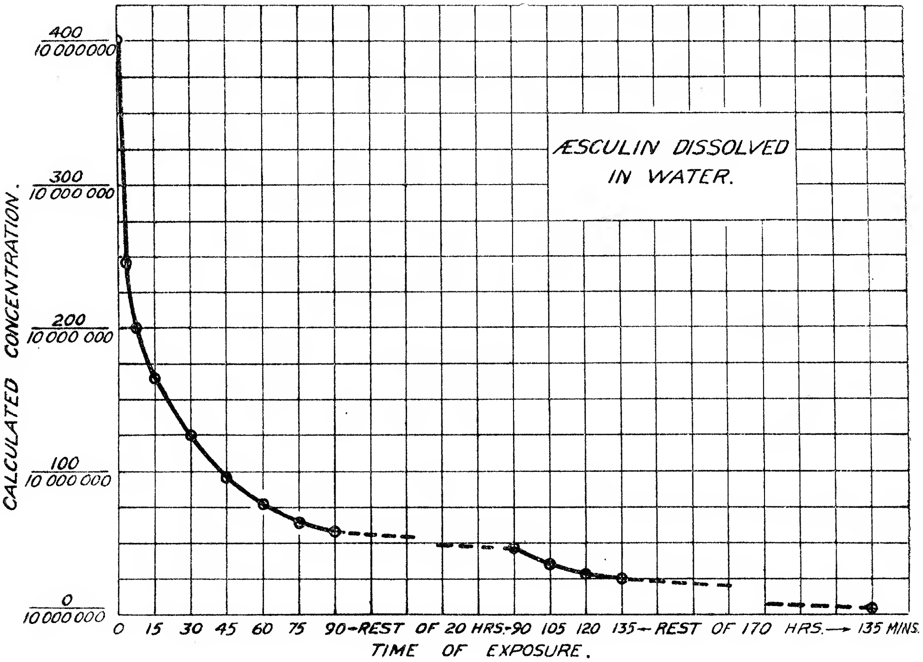
400/10 000 000
300/10 000 000
200/10 000 000
100/10 000 000
0/10 000 000
CALCULATED CONCENTRATION.
ÆSCULIN DISSOLVED IN WATER.
0 15 30 45 60 75 90→REST OF 20 HRS.→90 105 120 135→REST OF 170 HRS.→ 135 MINS.
TIME OF EXPOSURE.

Fig. 5.

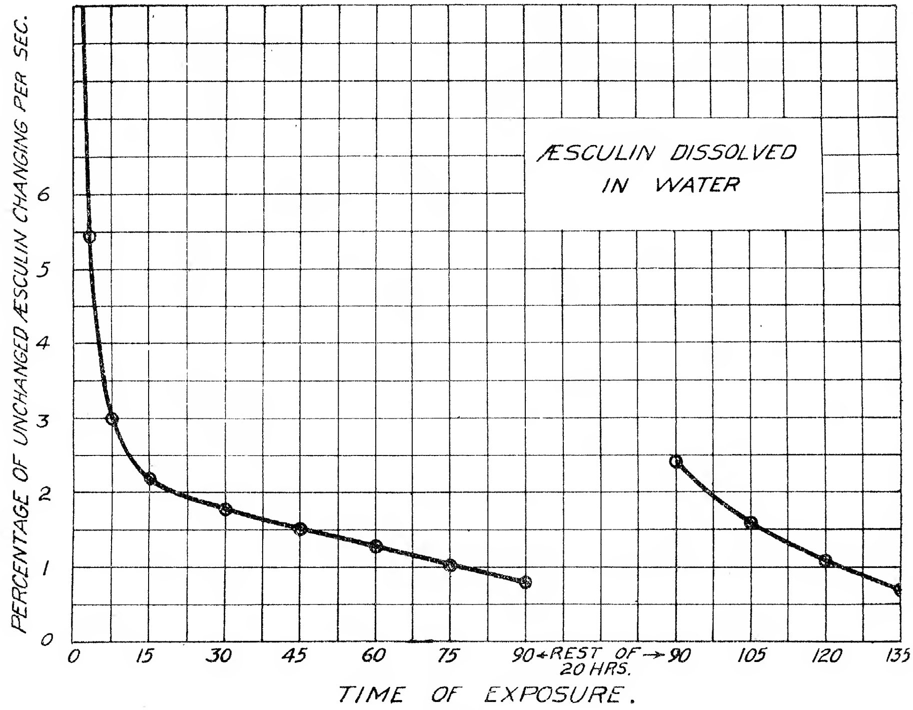
PERCENTAGE OF UNCHANGED ÆSCULIN CHANGING PER SEC.
6
5
4
3
2
1
0
ÆSCULIN DISSOLVED IN WATER
0 15 30 45 60 75 90←REST OF→90 105 120 135
20 HRS.
TIME OF EXPOSURE.

Fig. 6.

the initial stages of the exposure, but more slowly after the solution had been exposed for 15 minutes. For the period of the exposure from 15 to 90 minutes the percentage rate of transformation decreased proportionately with the time of the exposure.

Two points of interest that were revealed by these results are (1) that the solution continued to lose its fluorescent power during the periods of 20 hours and 170 hours that elapsed while it was in the cabinet in the darkened room, and (2) that when the exposure was resumed after the 20 hours' rest in darkness the percentage rate of transformation, as measured by the fluorescent power of the solution, was higher than it was a short time before it was placed in the cabinet at the cessation of the 90 minutes' exposure. This suggested that some product was formed during the exposures that prevented the solution from exhibiting its natural fluorescent power, that also continued to transform the æsculin when exposure ceased, and that finally disappeared during the rest period.

In a fifth set of experiments designed to throw light on this behaviour of aqueous solutions of æsculin exposed to ultra-violet light, it was found that when both dilute and strong solutions were exposed for short periods to ultra-violet light and then placed in the cabinet in the darkened room, the dilute solutions lost their fluorescent power completely in the course of two or three weeks, and the strong solutions in the course of two or three months. In the case of all solutions of æsculin that had lost completely their fluorescent power through exposure to ultra-violet light, it was found that their power of fluorescence was not restored by adding a small quantity of hydroxide to them.

VI. *Experiments with Oxygen and Ozone.*

In the experiments described above the solutions were always in contact with air during their exposure to ultra-violet light, and it was thought that oxygen, or possibly ozone, might have played some part in bringing about the results observed. To test the effect of oxygen on the solutions both air and oxygen were bubbled through them in darkness without the solutions showing any diminution in fluorescent power. Experiments were also made by bubbling both air and oxygen through the solutions in the presence of strong light from the quartz mercury arc lamp. In these experiments control solutions were used through which no gas was bubbled, and all the solutions were in glass vessels during exposure. Tests showed that the loss of fluorescent power was the same for the solutions through which the gases were bubbled as for the control solutions.

An experiment was then made in which oxygen was first passed through an ozoniser and then bubbled through the æsculin solution in darkness. In this case it was found that at the end of 5 minutes during which 270 c.c. of ozonised oxygen were bubbled through the solution the fluorescent power decreased to about 6 per cent. of its original value.

A complete set of readings showing the loss of fluorescent power due to bubbling ozonised oxygen through the æsculin solution were taken and a curve representing them is given in fig. 7. The total duration of the bubbling was only 10 minutes.

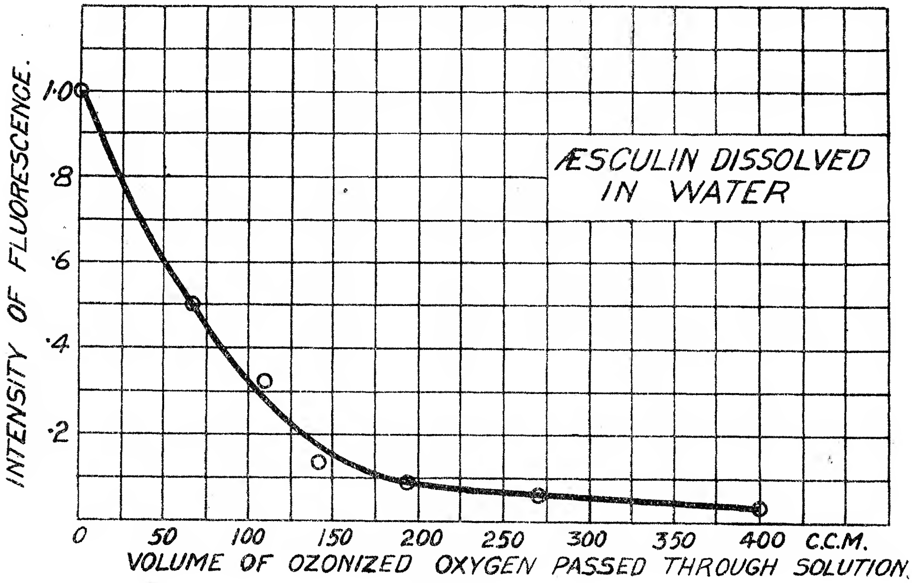

Fig. 7.

When ozonised oxygen was passed through a solution in complete darkness a faint luminescence was emitted by the liquid. With the standard solution, 4/100,000, the luminescence was just visible, but with stronger solutions (*e.g.*, 1/1000) the luminescence was quite distinct and of a bluish-white colour, much like the fluorescence of very dilute solutions of æsculin under the action of ultra-violet light. It was found that when these solutions of æsculin were completely transformed by the action of ozonised oxygen their fluorescent power was not restored by adding a hydroxide to them. In connection with the destruction of fluorescent power by ozone it should be stated that the total emission of light during the process of destruction was infinitesimal compared with the total emission of fluorescent light by solutions of the same initial strength while being transformed by ultra-violet light.

VII. *Experiments with Carbon Dioxide.*

Some experiments were made by bubbling carbon dioxide through solutions of æsculin. In these experiments the fluorescent power of the solutions gradually decreased with the passage through them of the gas. In one particular case, 270 c.c. of carbon dioxide were passed through a solution in 30 minutes and the fluorescent power dropped to 40 per cent. of its initial value. In this case, however, the phenomenon was different from that resulting from exposure to ultra-violet light and from that arising from treatment by ozone for the fluorescent power of the solution was completely restored by adding to it a few drops of alkali solution. The reaction with carbon dioxide was probably a simple acid one.

VIII. *Fluorescence of Æsculin Solutions in Sealed Vessels free of Air.*

(1) *Exposure in Glass Vessels.*—In these experiments the solutions to be exposed were boiled for about a minute to dispel all occluded gases and the glass tubes containing them were exhausted as highly as possible and sealed up. For the purpose of control a solution was boiled for the same time, then poured from one vessel to another to re-dissolve air into it, and finally put into a glass test tube and corked up without being exhausted. The control solution and those in the sealed tubes were placed symmetrically about and at the same distance from the lighted quartz mercury arc lamp. After exposure the seals were broken and the intensity of fluorescence of the solutions measured. A set of results obtained in this way is given in Table I.

Table I.

Solution.	Condition of experiment.	Time of exposure in hours.	Intensity of fluorescence at end of exposure.
A (control) ……	In corked glass test-tube	3·5	0·32
B ………………	Sealed in evacuated glass tube	3·5	1·00
C ………………	Sealed in evacuated glass tube	30·0	1·00

From these results it will be seen that in neither of the experiments did the solutions sealed in evacuated glass tubes show any indication of loss of fluorescent power through their exposure to the light from the mercury arc lamp. Throughout the whole time of their exposure they continued to fluoresce brilliantly.

(2) *Exposure in Quartz Vessels.*—In these experiments the fluorescent powers of the solutions were first measured and the solutions were then placed

in quartz tubes that were exhausted and sealed up. They were exposed to ultra-violet light in the same way as the solutions in the glass tubes. A set of results is given in Table II.

Table II.

Solution.	Condition of experiment.	Time of exposure (hours).	Intensity of fluorescence at end of exposure.
A	Sealed in evacuated quartz tube	2·0	0·19
B	,, ,, ,,	3·5	0·10
C	,, ,, ,,	26·0	0·19
D	,, ,, ,, (vacuum poor)	4·0	0·02

In these experiments it will be seen that the loss in fluorescent power was considerable. All of the solutions seemed to fluoresce much more brilliantly for the first minute or two of the exposure than they did for the remainder of it. The loss of fluorescent power by solution D was greater than that of the others, but its vacuum was found at the end of the exposure not to be good, and it may be that ozone produced by ultra-violet light from the oxygen of the air in it contributed to the result. The values of the intensity of fluorescence given in the fourth column of Table II for solutions A, C and D were found by breaking the seals of the quartz tubes at the end of the exposures and testing the solutions with the photometer in the manner indicated in the beginning of the paper. In the case of solution B, however, the intensity of fluorescence was measured at intervals while the solution was in the sealed quartz tube, the comparison being made with stock solution in a similar but unsealed and unevacuated quartz tube of the same wall thickness. The complete observations with solution B are recorded graphically in fig. 8. In the same figure a curve is given of the intensities of fluorescence of a control solution contained in an unsealed unexhausted quartz tube.

From the graph, B, it will be seen that for the first hour of exposure the decay of fluorescent power of the sealed solution was small in comparison with that of the unsealed one. The general form of the decay curves was, however, approximately the same in both cases for this period. At the end of the first hour of exposure the decay of the fluorescence of the sealed solution increased, and towards the end of the exposure proceeded approximately linearly with the duration of the exposure.

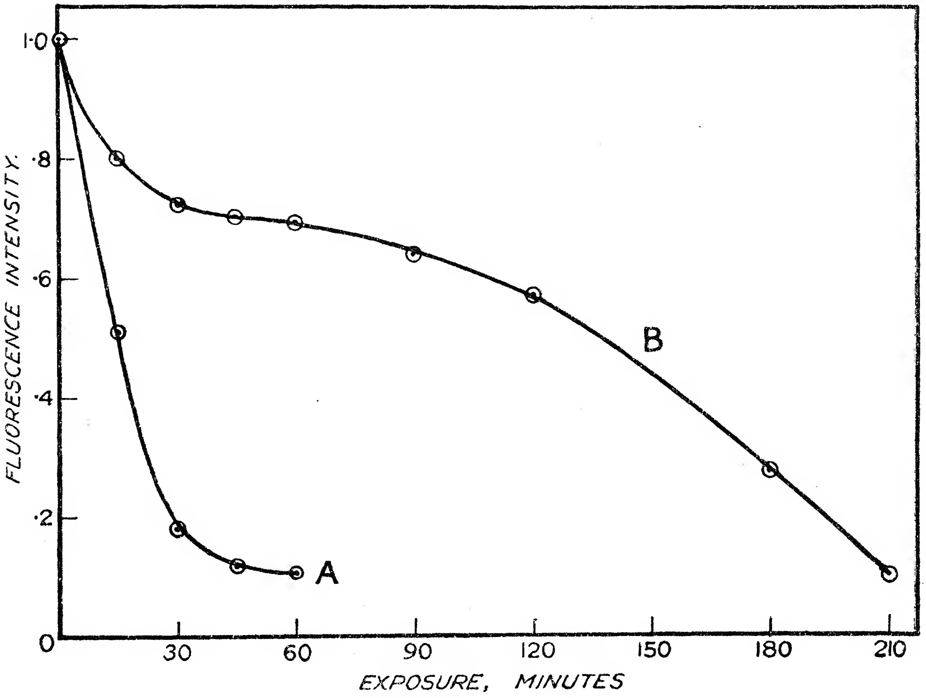

Fig. 8.

IX. *Results of the Investigation.*

The results of the experiments described above show that while the fluorescent power of solutions of æsculin in water can be destroyed by an acid (for example, carbon dioxide) the fluorescent power can be restored by the addition of a few drops of an alkali solution. It has also been shown that the fluorescent power of such solutions can be completely destroyed by passing through them ultra-violet light or ozonised oxygen. In such cases the fluorescent power cannot be restored by the addition of an alkali. The results also show that when ozonised oxygen is slowly bubbled through solutions of æsculin in water, the destruction of fluorescent power is accompanied by a faint luminescence. In this case the phenomenon would appear to be similar to the emission of light during the oxidation of phosphorus. It is also probably similar to the emission of light by decaying wood fibre or decaying organic matter in sea water.

Probably the most interesting results obtained from the investigation are those obtained from observations on the fluorescence of solutions of æsculin in water contained in exhausted sealed tubes. When the solutions were contained in glass tubes they could be made to fluoresce strongly for hours by violet or ultra-violet light in the range of longer wave-lengths, without exhibiting any loss in fluorescent power. When, however, they were exposed in sealed evacuated quartz tubes the fluorescent power was gradually and irrecoverably destroyed by ultra-violet light of the shorter wave-lengths.

The experiments on the fluorescence of aqueous solutions of æsculin contained in evacuated sealed glass tubes are of special importance, for they go to show that molecules of æsculin can be made to fluoresce strongly for hours without being destroyed when subjected to light of suitable wave-length. This result would seem to show that the view put forward by Perrin, namely, that the emission of fluorescent light by an organic substance is evidence of its destruction is not tenable generally.

The Propagation of Gravitational Waves.

By A. S. Eddington, F.R.S.

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1. The problem of the propagation of disturbances of the gravitational field was investigated by Einstein in 1916, and again in 1918.* It has usually been inferred from his discussion that a change in the distribution of matter produces gravitational effects which are propagated with the speed of light; but I think that Einstein really left the question of the speed of propagation rather indefinite. His analysis shows how the co-ordinates must be chosen if it is desired to represent the gravitational potentials as propagated with the speed of light; but there is nothing to indicate that the speed of light appears in the problem, except as the result of this arbitrary choice. So far as I know, the propagation of the absolute physical condition—the altered curvature of space-time—has not hitherto been discussed.

Weyl† has classified plane gravitational waves into three types, viz.: (1) longitudinal-longitudinal; (2) longitudinal-transverse; (3) transverse-transverse. The present investigation leads to the conclusion that transverse-transverse waves are propagated with the speed of light *in all systems of co-ordinates*. Waves of the first and second types have no fixed velocity—a result which rouses suspicion as to their objective existence. Einstein had also become suspicious of these waves (in so far as they occur in his special co-ordinate-system) for another reason, because he found that they convey no energy.

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* 'Berlin Sitzungsberichte,' p. 688 (1916); p. 154 (1918).

† 'Raum, Zeit, Materie,' 4th edition, p. 228; English edition, p. 252.